

AD-A112 059

FLUOROCHEM INC. AZUSA CA

SYNTHESIS OF FLUORINATED ACETYLENES. (U)

MAR 82 K BAUM, C D BEDFORD, R J HUNADI

F/6 7/3

N00014-78-C-0520

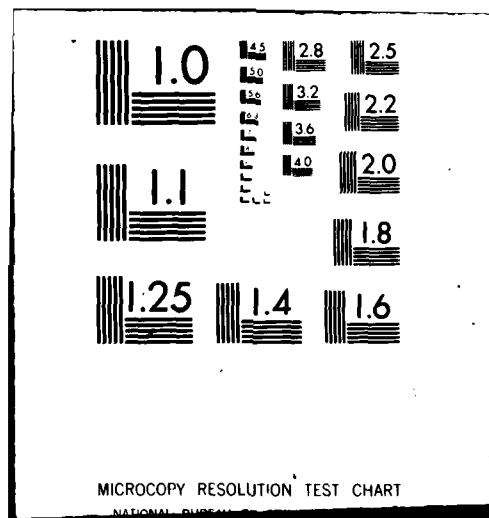
NL

UNCLASSIFIED

TR-3

1 or 1
26 3 2003

END
DATE
FILED
4-82
DTIC



ADA112059

(12)

OFFICE OF NAVAL RESEARCH
Contract N00014-78-C-0520
Task No. NR 356-688
TECHNICAL REPORT NO. 3

Synthesis of Fluorinated Acetylenes

by

Kurt Baum, Clifford D. Bedford and Ronald J. Hunadi

Prepared for Publication

in the

Journal of Organic Chemistry

Fluorochem, Inc.
680 S. Ayon Ave.
Azusa, CA 91702

March 1, 1982

Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited

Copy available to DTIC does not
permit fully legible reproduction

S MAR 17 1982 D
A

DTIC FILE COPY

8 16 070

DISCLAIMER NOTICE

**THIS DOCUMENT IS BEST QUALITY
PRACTICABLE. THE COPY FURNISHED
TO DTIC CONTAINED A SIGNIFICANT
NUMBER OF PAGES WHICH DO NOT
REPRODUCE LEGIBLY.**

Unclassified

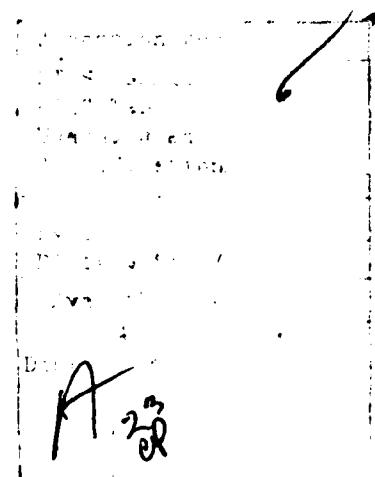
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE			READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 3	2. GOVT ACCESSION NO. AD-A112 059	3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) Synthesis of Fluorinated Acetylenes	5. TYPE OF REPORT & PERIOD COVERED Technical		
7. AUTHOR(s) Kurt Baum, Clifford D. Bedford and Ronald J. Hunadi	6. PERFORMING ORG. REPORT NUMBER N00014-78-C-0520		
9. PERFORMING ORGANIZATION NAME AND ADDRESS Fluorochem, Inc. 680 S. Ayon Ave. Azusa, CA 91702	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 356-688		
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Arlington, VA 22217	12. REPORT DATE 1 March 1982		
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	13. NUMBER OF PAGES 32		
	15. SECURITY CLASS. (of this report) Unclassified		
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE		
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited.			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES Submitted to Journal of Organic Chemistry			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Fluorocarbons; monomers; acetylenes; synthesis; MR spectra; IR spectra			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) New routes to fluorinated acetylenes were developed based on additions of iodofluorocarbons to silylacetylenes. Free radical addition of α , ω -diiodoperfluoroalkanes to trimethylsilylacetylene gave the iodotrimethylsilylolefins, $\text{Me}_3\text{SiIC}(\text{CF}_2)_n\text{CH}=\text{CISiMe}_3$, which reacted with potassium <i>t</i> -butoxide or DBU to give the trimethylsilylacetylenes, and with an excess of the base, the free diacetylenes. Perfluoroalkyl iodides similarly gave perfluoroalkyl acetylenes.			

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

The addition of perfluoroheptyl iodide to phenylacetylene, followed by treatment with potassium *t*-butoxide gave 1-phenylperfluorononyne. The peroxide catalyzed reaction of perfluoroalkyl iodides and bis(trimethylsilyl)acetylene gave 1:1 adducts, $R_F(Me_2SiCH_2I)C+CHSiMe_3$, resulting from intramolecular hydrogen abstraction by the initially formed vinyl radical. However, the thermal reaction of perfluoroalkyl iodides and diiodides with bis(trimethylsilyl)acetylene in the presence of free iodine gave the trimethylsilylacetylenes, which were desilylated with potassium fluoride. A route to diacetylenes was investigated based on addition of perfluoroiodo compounds to ethylene, dehydroiodination, bromination and elimination.



Unclassified

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

Synthesis of Fluorinated Acetylenes¹

Kurt Baum,* Clifford D. Bedford and Ronald J. Hunadi

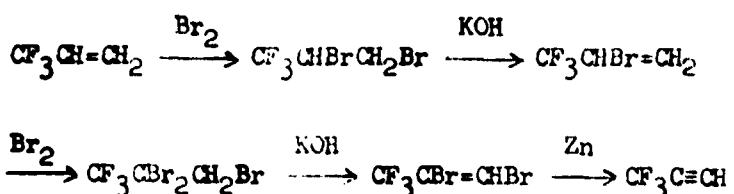
Fluorochem, Inc., Azusa, California 91702

Abstract

New routes to fluorinated acetylenes were developed based on additions of iodofluorocarbons to silylacetylenes. Free radical addition of α,ω -diiodoperfluoroalkanes to trimethylsilylacetylene gave the iodotrimethylsilylolefins, $\text{Me}_3\text{SiIC}=\text{CH}(\text{CF}_2)_n\text{CH}=\text{CISiMe}_3$, which reacted with potassium *t*-butoxide or DBU to give the trimethylsilylacetylenes, and, with an excess of the base, the free diacetylenes. Perfluoroalkyl iodides similarly gave perfluoroalkyl acetylenes. The addition of perfluoroheptyl iodide to phenylacetylene, followed by treatment with potassium *t*-butoxide gave 1-phenylperfluorononyne. The peroxide catalyzed reaction of perfluoroalkyl iodides and bis(trimethylsilyl)acetylene gave 1:1 adducts, $\text{R}_\text{F}(\text{Me}_2\text{SiCH}_2\text{I})\text{C}=\text{CHSiMe}_3$, resulting from intramolecular hydrogen abstraction by the initially formed vinyl radical. However, the thermal reaction of perfluoroalkyl iodides and diiodides with bis(trimethylsilyl)acetylene in the presence of free iodine gave the trimethylsilylacetylenes, which were desilylated with potassium fluoride. A route to diacetylenes was investigated based on addition of perfluoroiodo compounds to ethylene, dehydroiodination, brominations and eliminations.

Although perfluoroalkyl-substituted primary acetylenes have been known for three decades, perfluoroalkylene diacetylenes, $\text{HC}\equiv\text{C}(\text{CF}_2)_n\text{C}\equiv\text{CH}$, have not been reported. Haszeldine^{2,3} originally prepared 3,3,3-trifluoropropyne by the addition of trifluoromethyl iodide to acetylene (70-80%) followed by dehydrohalogenation (75%). Perfluoroethylacetylene was prepared similarly.⁴ Henne and Nager⁵ developed a high yield multistep route to 3,3,3-trifluoropropyne that avoided the use of acetylene under pressure; bromination of 3,3,3-trifluoropropene was followed by dehydrohalogenation, another bromination, dehydrohalogenation and dehalogenation (Scheme 1). More recently, this approach was used to prepare the perfluorobutyl, perfluorohexyl and perfluoroctyl analogs.⁶

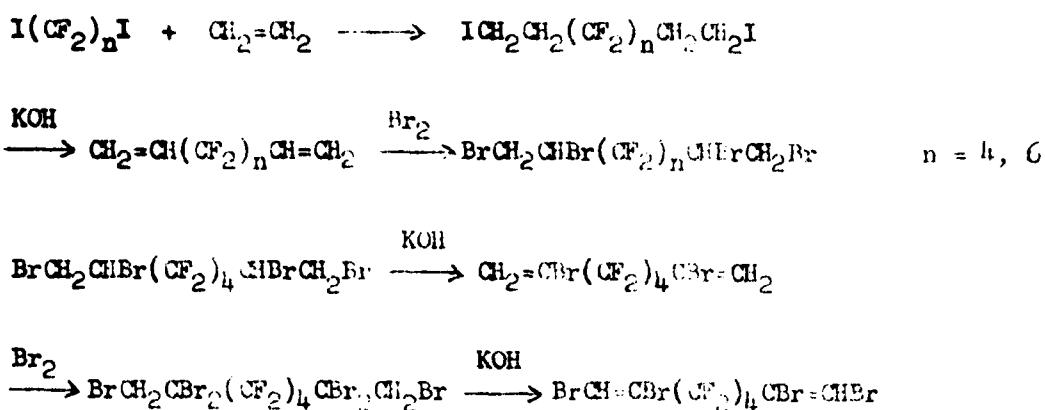
Scheme 1



Using α,ω -diiodoperfluoroalkanes as starting materials, available from the telomerization of tetrafluoroethylene with iodine,⁷ we approached the synthesis of α,ω -diacetylenes using Henne's sequence (Scheme 2). Reactions of ethylene with 1,4-diiodoperfluorobutane and 1,6-diiodoperfluorohexane, followed by dehydrohalogenations,⁸ have been reported to give the corresponding α,ω -diolefins. Bromine adducts of these olefins were obtained.

in 74-91% yield. The reaction of 3,3,4,4,5,5,6,6-octafluoro-1,2,7,8-tetrabromo-octane with potassium hydroxide in methanol gave 2,7-dibromo-3,3,4,4,5,5,6,6-octafluoro-1,7-octadiene. Another bromination followed by reaction with metha-

Scheme 2

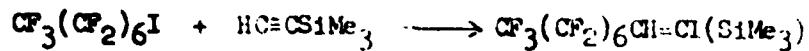
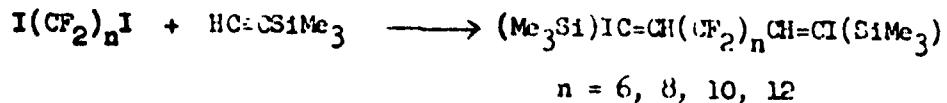


nolic potassium hydroxide gave a complex product mixture, the major component of which was isolated by GC and identified as the desired 1,2,7,8-tetrabromo-3,3,4,4,5,5,6,6-octafluoro-1,7-octadiene. Although moderately good yields were obtained for each step of the sequence, overall yields were poor. Therefore, this approach to diacetylenes was abandoned.

Trimethylsilylacetylene Additions. The trimethylsilyl group is a convenient blocking group for the synthesis of acetylenes. The synthesis of arylacetylenes has recently been reported using a palladium-catalyzed coupling of aromatic halides with trimethylsilylacetylene, followed by desilylation of the resulting arylacetylene derivatives with nucleophiles.^{9, 10}

We undertook the synthesis of fluorocarbon acetylenes by the free radical addition of iodofluorocarbons to trimethylsilylacetylene.

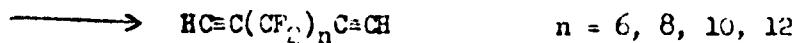
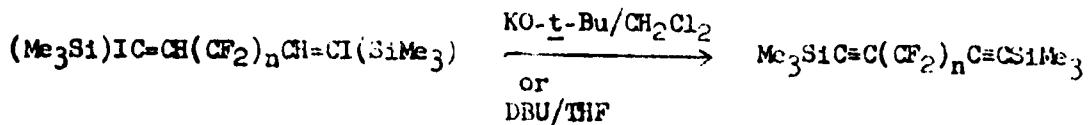
Treatment of 1,6-diiodoperfluorohexane with an excess of trimethylsilylacetylene in the presence of di-t-butyl peroxide at 120°C for 85 h gave a 92% yield of the diadduct, 3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,10-diido-1,10-bis(trimethylsilyl)-1,9-decadiene. With a reaction time of 47 h, a 73% yield was obtained of the corresponding product in which only one iodine of the 1,6-diiodoperfluorohexane was involved. A mixture of 1,8-diiodoperfluoroctane, 1,10-diiodoperfluorodecane and 1,12-diiodoperfluorododecane, readily obtained from the iodine-tetrafluoroethylene reaction, gave a 95% yield of the diadducts. Lower diiodides, however, did not readily give diadducts. Thus 1,4-diiodoperfluorobutane gave a complex mixture containing 33% of the monoadduct and 22% of the diadduct, based on GC analysis. Only the monoadduct was isolated from 1,2-diiodoperfluoroethane. A monofunctional starting material, perfluoroheptyl iodide, gave a 92% yield of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluoro-1-iodo-1-(trimethylsilyl)nonene.



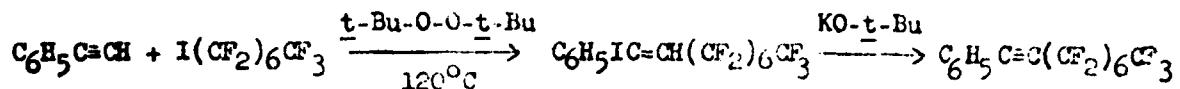
These trimethylsilyl iodo olefins were obtained as a mixture of E and Z isomers, separable by GC. Isomer assignments were based on NMR comparison with the hydrocarbon analogs. The vinyl proton of (E)-1-iodo-1-trimethylsilylhexene appears at δ 7.1 (t, $J_{HH} = 8$ Hz) and that of the (Z) isomer, at δ 6.1 (t, $J_{HH} = 6$ Hz). The respective values for the fluorinated compounds are δ 7.1 (t, $J_{HF} = 14-16$ Hz) and 6.8 ($J_{HF} = 10-13$ Hz). The silyl methyls for the (E) isomers appear as triplets whereas those of the (Z)-isomers appear as singlets.

The α -CF₂ groups of the (E)-isomers appear at δ 107-109 and those of the (Z)-isomers, at 111-113 ppm.

Dehydroiodination of these 1-iodo-1-(trimethylsilyl)olefins was quite sensitive to the types of basic reagents that were employed. The reaction of (Me₃Si)IC=CH(CF₂)_nCH=CI(SiMe₃) with methanolic potassium hydroxide at room temperature gave a 56.5% yield of ICH=CH(CF₂)_nCH=CHI, and attempts to dehydroiodinate this olefin were unsuccessful. The most satisfactory reagents to effect elimination to the silyl acetylene were potassium *t*-butoxide in methylene chloride at -20°C and DBU in tetrahydrofuran at -25°C. An excess of the reagents gave the free acetylene under the same conditions, or potassium fluoride could be used for the desilylation. The former reagent gave a 32.5% yield of HC≡C(CF₂)_nC≡CH from the iodo silyl olefin, and the latter, 45 to 72%. The analogous dodecadiyne, tetradecadiyne and hexadecadiyne were prepared from the mixture of the iodo silyl olefins described above, and penta-decafluorononyne was prepared similarly.



Another terminal acetylene that underwent free radical addition of an iodofluorocarbon was phenylacetylene. An adduct with perfluoroheptyl iodide was obtained in 89% yield, and its reaction with potassium *t*-butoxide in methylene chloride gave a 78% yield of the acetylene. Several adducts of fluorocarbon iodides with aliphatic acetylenes have been reported recently.¹²

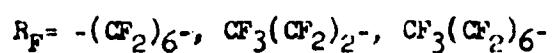
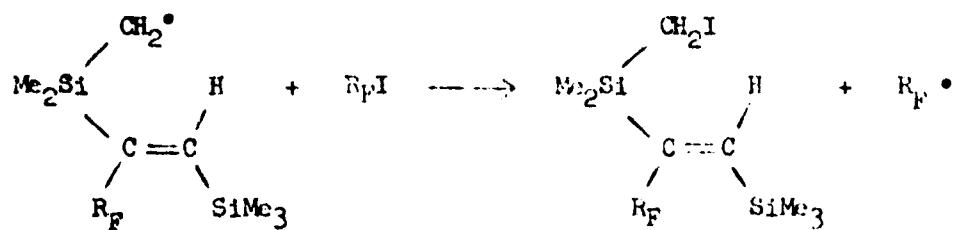
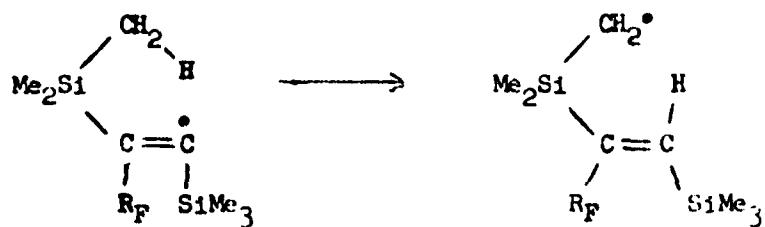
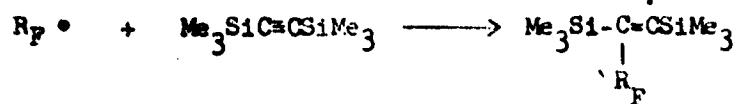
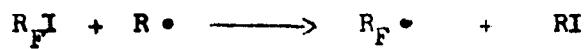


Bis(trimethylsilyl)acetylene Additions. In the formation of acetylenes from the adducts of fluorinated iodides with trimethylsilylacetylene, the ability of iodine to function as a leaving group is evidently enhanced by the adjacent silyl group. Accordingly, adducts of bis(trimethylsilyl)acetylene would be expected to provide acetylenes readily.

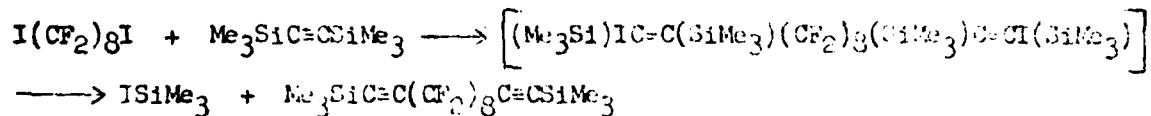
Iodofluorocarbons were found to react with bis(trimethylsilyl)acetylene at 120°C, in the presence of di-t-butyl peroxide, to give high yields of products that were shown to be 1:1 adducts by elemental analysis. Adducts were obtained from 1,6-diiodoperfluorohexane, perfluoropropyl iodide and perfluoroheptyl iodide in 75-85% yield. The NMR spectra, however, showed an olefinic hydrogen, and two silyl hydrogens shifted to δ 2.05-2.08. Evidently, free radical hydrogen transfer took place, as shown in Scheme 3.

Generally in free radical catalyzed iodide additions, a radical derived from the catalyst abstracts an iodine atom from the alkyl iodide and the resulting free radical adds to the unsaturated substrate. The new radical thus formed would normally abstract an iodine atom from the starting material to propagate the chain mechanism. In this case, however, the trimethylsilyl hydrogens are favorably situated for intramolecular hydrogen abstraction to give a silylmethylene radical. Abstraction of iodine from the starting material gives the observed product and regenerates a fluorocarbon radical. Intramolecular hydrogen abstractions of this type are well known in other systems.¹³

Scheme 3

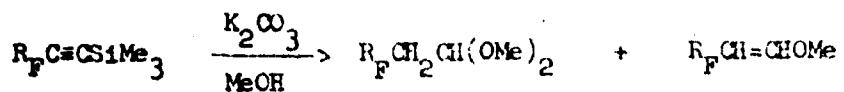
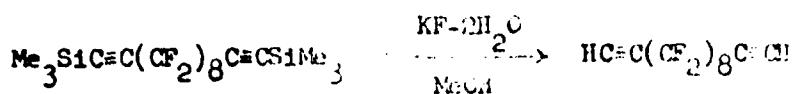


It was reasoned that this intramolecular hydrogen transfer might be averted if a better source of iodine radicals were available to trap the initially formed vinyl radicals. The desired reaction took place in the presence of a catalytic amount of elemental iodine at 200°C. Under these conditions, 1,8-diiodoperfluorooctane gave an 86% yield of 1,12-bis(trimethylsilyl)-perfluoro-1,11-dodecadiyne. Thus, the initial adduct spontaneously eliminated trimethylsilyl iodide to give the silylated acetylene

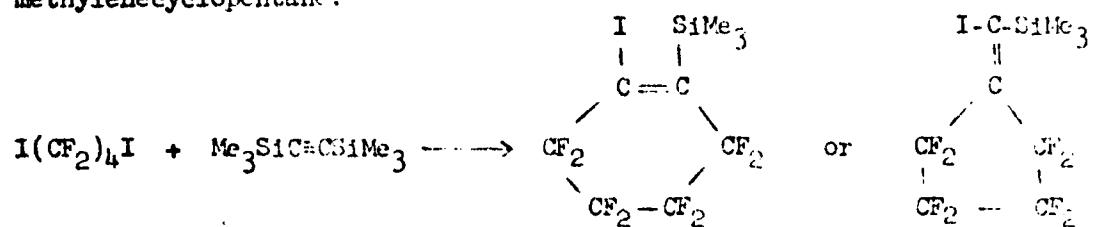


Monofunctional perfluoroalkyl iodides reacted similarly; 1-trimethylsilylperfluorononyne was isolated in 65% yield from perfluorooctyl iodide, whereas 1-trimethylsilylperfluorooctyne, 1-trimethylsilylperfluorodecyne and 1-trimethylsilylperfluorotetradecyne were obtained from a commercial mixture of perfluoroalkyl iodides.

1,12-Bis(trimethylsilyl)perfluoro-1,11-dodecadiyne was desilylated with potassium fluoride dihydrate to give a 79% yield of the free diacetylene. Potassium carbonate in methanol, the desilylation reagent of choice for arylsilylacetylenes,¹⁰ could not be used because of the susceptibility of the fluorinated acetylenes to nucleophilic additions. Thus, 1-(trimethylsilyl)perfluorononyne and methanol-potassium carbonate at room temperature gave a 73% yield of 1,1-dimethoxy-3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluorononane and an 11% yield of the 1-methoxynonene. The reaction of trifluoropropyne with sodium alkoxides to give 3,3,3-trifluoro-1-alkoxypropanes has been reported.¹⁴



Reactions of lower diiodides with bis(trimethylsilyl)acetylene were complicated by the formation of cyclic products by the involvement of both iodine functions with the same acetylene molecule. The 1,4-diiodoperfluorobutane gave an 81% yield of a product with elemental analysis consistent with 1-iodo-2-(trimethylsilyl)perfluorocyclohexene, or its isomer, iodo(trimethylsilyl)-methylenecyclopentane.



The corresponding cyclic adduct, as well as 1,10-bis(trimethylsilyl)perfluoro-1,9-decadiyne, was obtained from 1,6-diiodoperfluorohexane. The ratio of these products was a function of the amount of bis(trimethylsilyl)acetylene used. The ratio of acetylenic product to cyclic olefin varied from 0.3 for equimolar amounts of the starting materials to 7.5 for a fourfold excess of bis(trimethylsilyl)acetylene. As is the case for the above example, the spectral evidence does not clearly differentiate between the exocyclic and endocyclic olefin structures for the cyclic adduct.

Thus, perfluoroalkyl acetylenes as well as α,ω -perfluoroalkylene diacetylenes are available from iodofluorocarbon reactions with trimethylsilylacetylene and with bis(trimethylsilyl)acetylene. Trimerization and polymerization studies with these acetylenes will be reported elsewhere.

Experimental Section

A Varian 920 chromatograph with a 10 ft x 3/8 in. column of 10% QF-1 on acid-washed Chromosorb W was used for both analytical and preparative gas chromatography. NMR spectra were obtained with a Varian T-60 spectrometer, and IR spectra, with a Perkin-Elmer 700 spectrometer.

3,3,4,4,5,6,6-Octafluoro-1,0-_a1-iodooctane. Ethylene (0.050 mol) was condensed at -130°C (n-pentane liquid nitrogen bath) into a 75 mL Monel cylinder containing 11.4 g (0.025 mol) of 1,4-diiodoperfluorobutane and 0.2 mL of dibutyl peroxide. The cylinder was sealed and heated for 22 h at 130°C. The product was extracted with two 50 mL portions of methylene chloride and the solution was washed with two 25 mL portions of 0.1 N sodium thiosulfate and dried over magnesium sulfate. Removal of the solvent gave 10.4 g (82%) of white solid. An analytical sample was recrystallized from methanol: mp 89-91°C; ¹H NMR (CDCl₃) δ 2.08 (m, 4 H, CH₂), 3.16 (m, 4 H, CH₂I); ¹⁹F NMR (CDCl₃) δ 118.0 (t, 4 F, J=11.3 Hz, CF₂), 126.0 ppm (t, 4 F, J=11.3 Hz, CF₂).

Anal. Calcd for C₈H₈F₈I: C, 18.84; H, 1.58; Found: C, 18.70; H, 1.65.

3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluoro-1,10-diiododecane. The above procedure using 1,6 diiodoperfluorohexane gave a 76% yield of white solid, mp 69-71°C: ¹H NMR (CDCl₃) δ 2.60 (m, 4 H, CH₂), 3.16 (m, 4 H, CH₂I); ¹⁹F NMR (CDCl₃) δ 116.4 (m, 4 F, CF₂), 124.8 (m, 4 F, CF₂), 123.2 ppm (m, 4 F, CF₂).

3,3,4,4,5,5,6,6-Octafluoro-1,7-octadiene. A solution of 20 g (0.039 mol) of 3,3,4,4,5,5,6,6-octafluoro-1,8-diiodooctane and 4.5 g of potassium hydroxide in 15 mL of ethylene glycol was heated with stirring at 140°C. The product, 7.25 g (73%) of colorless oil, bp 82-87°, distilled from the reaction mixture as it was formed. An analytical sample was isolated by GC: ¹H NMR (CDCl₃) δ 5.6-5.9 (m, 6 H, CH₂=CH); ¹⁹F NMR (CDCl₃) δ 115.7 (m, 4 F, CF₂), 124.8 ppm (t, 4 F, J=11.3 Hz, CF₂).

Anal. Calcd for $C_8H_6F_8$: C, 37.81; H, 2.38; Found: C, 37.55; H, 2.10.

3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluoro-1,9-decadiene. The above procedure using 1,10-diiodo-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluorodecane gave an 87% yield of 3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,9-decadiene, bp 135-137°C: 1H NMR ($CDCl_3$) δ 5.5-5.8 (m, 2 H, $CH_2=CH$); ^{19}F NMR ($CDCl_3$) δ 116.8 (m, 4 F, CF_2), 126.4 (m, 4 F, CF_2), 124.1 ppm (m, 4 F, CF_2).

Anal. Calcd for $C_{10}H_6F_{12}$: C, 33.92; H, 1.71; Found: C, 33.66; H, 1.80.

3,3,4,4,5,5,6,6-Octafluoro-1,2,7,8-tetrabromoocetane. A solution of 6.0 g (0.023 mol) of 3,3,4,4,5,5,6,6-octafluoro-1,7-octadiene and 2.56 mL (0.046 mol) of bromine in 10 mL of chloroform was irradiated with a Par lamp for 1 h. Methylene chloride (20 mL) was added and the solution was washed with two 10 mL portions of 1 N sodium thiosulfate and dried over magnesium sulfate. Removal of solvent under vacuum gave 10.05 g (74%) of a white solid. Recrystallization from methanol afforded an analytical sample, mp 32-34°C: 1H NMR ($CDCl_3$) δ 3.72 (m, 4 H, CH_2Br), 4.24 (m, 2 H, $CHBr$); ^{19}F NMR ($CDCl_3$) δ 114.7 (m, 4 F, CF_2), 121.6 ppm (m, 4 F, CF_2).

Anal. Calcd for $C_8H_6F_6Br_4$: C, 16.75; H, 1.05; Br, 55.71; Found: C 16.76; H, 0.99; Br, 55.40.

3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluoro 1,2,9,10-tetrabromodecane. Bromination of 3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,9-decadiene by the above method gave a 91% yield of the solid product, mp 43-45°C: 1H NMR ($CDCl_3$) δ 3.59 (m, 4 H, CH_2Br); 4.20 (m, 2 H, $CHBr$); ^{19}F NMR ($CDCl_3$) δ 114.8 (m, 4 F, CF_2), 121.7 (m, 4 F, CF_2), 124.4 ppm (m, 4 F, CF_2).

Anal. Calcd for $C_{10}H_6F_{12}Br_4$: C, 17.83; H, 0.90; Found: C, 18.01; H, 0.98.

2,7-Dibromo-3,3,4,4,5,5,6,6-octafluoro-1,7-octadiene. A solution of 1.5 g of potassium hydroxide and 7.0 g (0.012 mol) of 3,3,4,4,5,5,6,6-octa-

fluoro-1,2,7,8-tetrabromoocetane in 15 mL of methanol was heated with stirring for 1 h at 60°C. The product was diluted with 50 mL of methylene chloride, washed with 2-50 mL portions of water, dried over sodium sulfate and stripped of solvent under vacuum to give 3.8 g (75%) of a colorless oil. An analytical sample was isolated by GC: ^1H NMR (CDCl_3) δ 6.16 (m, 2 H, $J_{\text{H},\text{H}} = 3.0$ Hz, $\text{C}(\text{H})_2$) 6.42 (d, 2 H, $J_{\text{H},\text{H}} = 3.0$ Hz, $\text{C}(\text{H})_2$); ^{19}F NMR (CDCl_3) δ 110.8 (t, 4 F, $J_{\text{F},\text{F}} = 11.3$ Hz, CF_2), 122.0 ppm (t, 4 F, $J_{\text{F},\text{F}} = 11.3$ Hz, CF_2).

Anal. Calcd for $\text{C}_8\text{H}_4\text{F}_8\text{Br}_4$: C, 23.33; H, 0.98; Found: C, 23.6%; H, 0.91.

1,2,7,8-Tetrabromo-3,3,4,4,5,5,6,6-octafluoro-1,7-octadiene. A solution of 2.4 g (0.0058 mol) of 2,7-dibromo-3,3,4,4,5,5,6,6-octafluoro-1,7-octadiene and 1.86 g (0.0106 mol) of bromine in 15 mL of chloroform was irradiated with a Par lamp for 1 h. The mixture was diluted with 20 mL of methylene chloride, washed with 2-10 mL portions of 1 N sodium thiosulfate, dried over magnesium sulfate and stripped of solvent under vacuum to give 2.9 g of white solid. This solid was stirred for 1 h with a solution of 0.5 g of potassium hydroxide in 15 mL of methanol. The mixture was added to 25 mL of water and the product extracted with 35 mL of methylene chloride. The methylene chloride solution was washed with 50 mL of water, and dried. Solvent was removed to give 1.2 g of an oil. GC showed a complex mixture from which the major component was trapped and identified as 1,2,7,8-tetrabromo-3,3,4,4,5,5,6,6-octafluoro-1,7-octadiene: ^1H NMR (CDCl_3) δ 7.45 ppm (br s, CR); ^{19}F NMR (CDCl_3) δ 108.0 (t, 4 F, CF_2), 121.2 ppm (t, 4 F, CF_2).

Anal. Calcd for $\text{C}_8\text{H}_2\text{F}_8\text{Br}_4$: C, 16.87; H, 0.35. Found: C, 17.09; H, 0.50.

3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluoro-1,10-diiodo-1,10-bis(trimethylsilyl)-1,9-decadiene. A mixture of 3.3 g (6.0 mmol) of 1,6-diiodoperfluorohexane, 1.5 g of trimethylsilylacetylene and 0.5 mL of di-t-butyl peroxide was heated in a sealed glass tube under nitrogen for 65 hrs at 120°. The product was dissolved in 50 mL of methylene chloride, dried over magnesium sulfate and stripped of solvent under vacuum to give 4.2 g (92%) of the title compound as a mixture of E/E, Z/Z and E/Z isomers, analytically pure without further treatment: proton NMR CDCl_3 δ 7.23 (t, $J_{\text{HF}} = 15$ Hz, =CH-, E isomers), δ 6.60 (t, $J_{\text{HF}} = 13$ Hz, =CH-, Z isomers) 0.35 (t, CH_3Si , E isomers) and 0.25 ppm (s, CH_3Si , Z isomers); ^{19}F NMR (CDCl_3) δ 108.4 (m, =CH- CF_2 -, E isomers), 111.6 (m, =CH- CF_2 , Z isomers), 123.2 (m, CF_2 internal) and 124.4 ppm (m, =CH- CF_2CF_2).

Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{F}_{10}\text{I}_2\text{Si}_2$: C, 25.61; H, 2.69; F, 30.39; I, 33.83. Found: C, 25.52; H, 2.60; F, 30.15; I, 33.67.

3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluoro-1,8-diiodo-1-trimethylsilyloctene. When a heating period of only 47 h at 120°C was used with the above reactants, a 72% yield of the monoadduct was obtained as a 70:30 mixture of E and Z isomers. The isomers were separated by GC: E isomer 'H NMR (CDCl_3) δ 7.15 (t, 1 H, $J_{\text{H,F}} = 14$ Hz, CH), 0.35 ppm (t, 9 H, CH_3); ^{19}F NMR (CDCl_3) δ 65.3 (t, 1 s, CF_2I), 108.4 (q, 2 F, CF_2), 123.2 (m, 2 F, CF_2), 124.8 (m, 4 F, CF_2), 124.4 ppm (m, 2 F, CF_2).

Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{F}_{10}\text{I}_2\text{Si}$: C, 20.26; H, 1.55; F, 34.96; I, 38.92. Found: C, 20.25; H, 1.57; F, 34.76; I, 38.66.

Z-isomer 'H NMR (CDCl_3) δ 6.70 (t, 1 H, $J_{\text{H,F}} = 13$ Hz, CH), 0.25 ppm (s, 9 H,

CH_3); ^{19}F NMR (CDCl_3) δ 65.6 (t, 2 F, CF_2 I), 111.6 (q, 2 F, CF_2), 115.2 (m, 2 F, CF_2), 122.8 (m, 4 F, CF_2), 124.4 ppm (m, 2 F, CF_2).

Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{F}_{12}\text{I}_2\text{Si}$: C, 20.26; H, 1.55; F, 34.96; I, 38.92. Found: C, 20.21; H, 1.52; F, 34.69; I, 38.85.

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-Hexadecafluoro-1,12-diido-1,12-bis(trimethylsilyl)-1,11-dodecadiene, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12-eicosfluoro-1,14-diido-1,14-bis(trimethylsilyl)-1,13-tetradecadiene, and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14-tetraeicosfluoro-1,16-diido-1,16-bis(trimethylsilyl)-1,15-hexadecadiene. Treatment of 16.35 g (0.025 moles) of a mixture of 1,8-diiodoperfluorooctane, 1,10-diiodoperfluorodecane and 1,12-diiodoperfluorododecane with 5 g of trimethylsilylacetylene and 2.5 mL of di-t-butyl peroxide by the above procedure yielded, after 48 hrs of heating, 16.1 g (95%) of a mixture of the title compounds, as an equal mixture of E and Z isomers: ^1H NMR (CDCl_3) δ 7.25 (t, 2 H, $J_{\text{HF}} = 15$ Hz, =CH, E isomer), 6.70 (t, 2 H, $J_{\text{HF}} = 13$ Hz, =CH, Z isomer) 0.33 (t, 18 H, SiCH_3 , E isomer) and 0.27 ppm (s, 18 H, SiCH_3 , Z isomer); ^{19}F NMR (CDCl_3) δ 108.4 (m, 4 F, CH-CF_2 , E isomer) 111.6 (m, 4 F, CHCF_2 , Z isomer), 123.2 (m, CF_2 internal) and 124.2 ppm (m, =CH- CF_2 - CF_2).

3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Pentadecafluoro-1-iodo-1(trimethylsilyl)-nonene. A mixture of 3.0 g (6.0 mmol) of perfluorohexyl iodide, 0.60 g (6.0 mmol) of trimethylsilylacetylene and 0.5 mL of di-t-butyl peroxide was sealed in a glass tube under nitrogen and heated at 120°C for 48 hrs. The product was dissolved in methylene chloride, and dried over magnesium sulfate. Removal of solvent under vacuum gave 3.31 g (92%) of a colorless oil, which proved to be an equal mixture of E and Z isomers of the title compound. The isomers were separated by

E isomer proton NMR (CDCl_3): δ 7.10 (t, 1 H, $J_{\text{HF}} = 15$ Hz, $=\text{CH}$), 0.33 ppm (t, 9 H, SiCH_3); ^{19}F NMR (CDCl_3) δ 85.2 (t, 3 F, CF_3), 108.4 (q, 2 F, $=\text{CH}-\text{CF}_2$), 124 (m, 8 F, CF_2) and 127.6 ppm (m, 2 F, $=\text{CHCF}_2\text{CF}_2$); Z isomer proton NMR (CDCl_3) δ 6.58 (t, $J_{\text{HF}} = 12$ Hz, 1 H, $=\text{CH}$), 0.25 ppm (s, 9 H, SiCH_3); ^{19}F NMR (CDCl_3) δ 85.2 (t, 3 F, CF_3), 111.8 (q, 2 F, $=\text{CHCF}_2$), 124 (m, 8 F, CF_2) and 127.6 ppm (m, 2 F, $=\text{CHCF}_2\text{CF}_2$).

Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{F}_{15}\text{Si}$: C, 24.14; H, 2.19; F, 47.72; I, 21.25.
Found: C, 23.93; H, 1.99; F, 47.60; I, 21.57.

Reaction of 1,4-Diodoperfluorobutane with Trimethylsilylacetylene. A mixture of 1.4 g (3.0 mmol) of 1,4-diiodoperfluorobutane, 0.90 g (9.2 mmol) of trimethylsilylacetylene and 0.2 g (1.4 mmol) of di-t-butyl peroxide was heated in a sealed tube for 6 days at 120°C. GC analysis (150-185°C) showed 7 components, 12%, 23%, 20%, 13%, 6%, 22% and 3% of the sample, respectively. The first component consisted of 1,4-diiodoperfluorobutane and trimethylsilylacetylene. The second, fifth and last components were not identified. The third component identified as (E)-1,4-difido-1-trimethylsilyl-3,3,4,4,5,5,6,6-octafluorohexene: ^1H NMR (CDCl_3) δ 7.12 (t, $J_{\text{HF}} = 15$ Hz, 1 H, $=\text{C}-\text{H}$), 0.35 ppm (t, $J = 1.5$ Hz 9 H, CH_3); ^{19}F NMR (CDCl_3) δ 64.8 (t, 2 F, $-\text{CF}_2\text{I}$), 108.2 (q, 2 F, $-\text{CF}_2-\text{C}(\text{H})=\text{C}$), 114.8 (m, 2 F, CF_2), 123.4 ppm (t, 2 F, CF_2).

Anal. Calcd for $\text{C}_9\text{H}_{10}\text{F}_8\text{I}_2\text{Si}$: C, 19.58; H, 1.83; F, 27.53; I, 45.98.
Found: C, 19.70; H, 1.76; F, 27.39; I, 45.70.

The fourth fraction consisted of a 1:1.5 (E)/(Z) isomer mixture of the above compound. Assignments for the Z isomer are as follows: ^1H NMR (CDCl_3) δ 6.60 (t, $J_{\text{H},\text{F}} = 12$ Hz, 1 H, $\text{C}=\text{CH}$), 0.22 ppm (s, 9 H, $-\text{CH}_3$); ^{19}F NMR (CDCl_3)

δ 64.8 (t, 2 F, $-\text{CF}_2\text{I}$), 112.0 (q, 2 F, $-\text{CF}_2\text{C}(\text{H})=\text{C}$), 114.8 (m, 2 F, CF_2), 123.4 (t, 2 F, CF_2). The sixth component was an (E/E)/(Z/Z)/(E/Z) mixture of 3,3,4,4,5,5,6,6-octafluoro-1,8-diioda-1,8-bis(trimethylsilyl)-1,7-octadiene: ^{19}F NMR (CDCl_3) δ 116.9 (m, 2 F, $-\text{CF}_2\text{C}(\text{H})=\text{C}$, E-isomer), 117.9 (m, 2 F, $-\text{CF}_2\text{C}(\text{H})=\text{C}$, Z-isomer), 120.0 (m, 2 F, CF_2), 132.1 (m, 2 F, CF_2), 134.0 ppm (m, 2 F, CF_2); IR (film) 3005 (s i CH_3), 2950 (s i CH_3), 1585 cm^{-1} (C=CH).

Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{F}_8\text{I}_2\text{Si}_2$: C, 25.86; H, 3.10; F, 23.37. Found: C, 26.17; H, 3.01; F, 23.81.

Reaction of Tetrafluoro-1,2-diiodoethane with Trimethylsilylacetylene.

A mixture of 0.106 g (0.30 mmol) of tetrafluoro-1,2-diiodoethane, 0.088 g (0.90 mmol) of trimethylsilylacetylene and 0.007 g (0.05 mmol) of di-t-butyl peroxide was heated in a sealed tube for 36 h at 120°C and 25 h at 150°C . GC (130°C) showed that the major product was (E) and (Z)-3,3,4,4-tetrafluoro-1,4-diiodo-1-trimethylsilylbutene: (E) isomer ^1H NMR (CDCl_3) δ 7.31 (t of t, $J = 14.5$ and 1 Hz, 1 H, $\text{CF}_2\text{C}(\text{H})=\text{C}$), 0.36 ppm (t, $J = 1$ Hz, 9 H, SiCH_3); ^{19}F NMR (CDCl_3) δ 66.2 (t, $J_{\text{FF}} = 8$ Hz, 2 F, ICF_2^-), 102.8 ppm (m, 2 F, $\text{ICF}_2\text{CF}_2^-$); (Z) isomer ^1H NMR (CDCl_3) δ 6.79 (t of t, $J = 12$ and 1 Hz, 1 H, $\text{CF}_2\text{C}(\text{H})=\text{C}$, 0.31 ppm (s, 9 H, $-\text{SiCH}_3$); ^{19}F NMR (CDCl_3) δ 66.8 (t, $J_{\text{FF}} = 10$ Hz, 2 F, ICF_2^-), 107.0 ppm (m, 2 F, $\text{ICF}_2\text{CF}_2^-$).

Anal. Calcd for $\text{C}_7\text{H}_{10}\text{F}_4\text{I}_2\text{Si}$: C, 18.60; H, 2.23. Found: C, 18.65; H, 2.05.

3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluoro-1,10-diiodo-1,9-decadiene. A solution of 0.5 g of potassium hydroxide and 1.0 g (1.3 mmol) of 3,3,4,4,5,5,6,6,

7,7,8,8-dodecafluoro-1,10-diido-1,10-bis(trimethylsilyl)-1,9-decadiene in 20 mL of methanol was allowed to stand for 18 h. The solution was diluted with 100 mL of water and the product was extracted with 2-50 mL portions of methylene chloride, washed with water, dried over magnesium sulfate and stripped of solvent to give 0.46 g (56.5%) of a pale yellow oil that solidified on standing. An analytical sample was obtained by GC: mp 42.44°C; ^1H NMR (CDCl_3) δ 7.22 (2 H, $J_{\text{HH}} = 16$ Hz, $J_{\text{HF}} = 1$ Hz, CHI), 6.60 ppm (2 H, $J_{\text{HH}} = 16$ Hz, $J_{\text{HF}} = 12$ Hz, CH); ^{19}F NMR (CDCl_3) ϕ 113.6 (m, 4 F, CF_2), 122.8 (m, 4 F, CF_2), 124.4 ppm (m, 4 F, CF_2).

Anal. Calcd for $\text{C}_{10}\text{H}_4\text{F}_{12}\text{I}_2$: C, 19.82; H, 0.66; F, 37.62; I, 41.89. Found: C, 19.93; H, 0.72; F, 37.40; I, 41.78.

3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluoro-1,9-decadiyne. A mixture of 15 g of potassium *t*-butoxide and 250 mL of methylene chloride was stirred under nitrogen at -20°C and 12.8 g (0.017 mole) of 1,10-diido-1,10-bis(trimethylsilyl)-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,9-decadiene was added dropwise. The slurry was stirred for 1 hr at -20° and for 4 hrs at 0°, and then 100 mL of 3 N hydrochloric acid was added. The mixture was stirred for 1 h, and the organic layer was washed with water, dried and distilled to give 1.92 g (32.5%) of the title compound, bp 55-59° (15-20 mm): ^1H NMR (CDCl_3) δ 2.93 ppm (t, 2 H, $J_{\text{HF}} = 4.5$ Hz, CH); ^{19}F NMR (CDCl_3) ϕ 102 (m, 4 F, α - CF_2), 123.0 (m, 4 F, δ - CF_2) and 124.4 ppm (m, 4 F, β - CF_2); IR 3350 (CH), 2200 (C≡C) and 1165 cm^{-1} (CF_2).

Anal. Calcd for $\text{C}_{10}\text{H}_2\text{F}_{10}$: C, 34.31; H, 0.57. Found: C, 34.08; H, 0.56.

Alternatively, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was used for the

elimination. To a solution of 20.0 g (0.0256 mol), of 3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,10-diido-1,10-bis(trimethylsilyl)-1,9-decadiene in 160 mL of freshly distilled tetrahydrofuran at -25°C under nitrogen was added, over a 10 min period, 8.8 mL (0.08 mol) of DBU. The mixture was stirred for 1.5 h at -25°C and was filtered. The precipitate was washed with pentane and the combined solutions were washed with saturated sodium chloride solution and filtered through a short column of basic alumina. Distillation gave the diacetylene in 45 to 72% yield.

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-Hexadecafluoro-1,11-dodecadiyne, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12-Eicosfluoro-1,13-tetradecadiyne, and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14-Tetraeicosafuoro-1,15-hexadecadiyne. A slurry of 3 g (26 mmol) of potassium *t*-butoxide in 40 mL of methylene chloride was stirred under nitrogen at -20°C while 8.2 g of a solution of $(\text{CH}_3)_3\text{SiIC=CH}(\text{CF}_2)_8\text{CH=CHSi}(\text{CH}_3)_3$, $(\text{CH}_3)_3\text{SiIC=CH}(\text{CF}_2)_{10}\text{CH=CHSi}(\text{CH}_3)_3$, and $(\text{CH}_3)_3\text{SiIC=CH}(\text{CF}_2)_{12}\text{CH=CHSi}(\text{CH}_3)_3$ in 20 mL of methylene chloride was added dropwise. The reaction mixture was stirred for 1 h at -20°C and for 3 h at 0°C. Potassium fluoride (1.5 g) and 25 mL of *t*-butanol were then added and the mixture was stirred for 3 h at ambient temperature. Methylene chloride (100 mL) was added and the solution was washed with five 100 mL portions of water, dried over magnesium sulfate and stripped of solvent. The residue, analyzed by GC, was shown to contain 1.3 g of $\text{HC}\equiv\text{C}(\text{CF}_2)_8\text{C}\equiv\text{CH}$, 0.73 g of $\text{HC}\equiv\text{C}(\text{CF}_2)_{10}\text{C}\equiv\text{CH}$ and 0.22 g of $\text{HC}\equiv\text{C}(\text{CF}_2)_{12}\text{C}\equiv\text{CH}$ (total yield 50%). Analytical samples were isolated by GC.

Hexadecafluoro-1,11-dodecadiyne, $\text{HC}\equiv\text{C}(\text{CF}_2)_8\text{C}\equiv\text{CH}$ was a colorless liquid: proton NMR (CDCl_3) δ 2.94 ppm (t, $J_{\text{HF}} = 4.5$ Hz, 21); ^{19}F NMR (CDCl_3) ϕ 102

(m, 4 F, α -CF₂), 122.8 (m, 8 F, internal fluorines) and 124 ppm (m, 4 F, β -CF₂); IR 3355 (CH), 2195 (C≡C) and 1190 cm⁻¹ (CF₂).

Anal. Calcd for C₁₂H₂F₁₆: C, 32.02; H, 0.45. Found: C, 32.44; H, 0.55.

Eicosfluoro-1,13-tetradecadiyne, HC≡C(CF₂)₁₀C≡CH, was a colorless oil: ¹H NMR (CDCl₃) δ 2.94 ppm (t, J_{HF} = 4.5 Hz, CH); ¹⁹F NMR (CDCl₃) ϕ 102 (m, 4 F, α -CF₂), 122.8 (m, 12 F, internal F) and 124.2 ppm (m, 4 F, β -CF₂); IR 3355 (CH), 2200 (C≡C) and 1195 cm⁻¹ (CF₂).

Anal. Calcd for C₁₄H₂F₂₀: C, 30.57; H, 0.37; F, 69.07. Found: C, 30.27; H, 0.38; F, 68.84.

Tetraicosfluoro-1,15-hexadecadiyne, HC≡C(CF₂)₁₂C≡CH, was a white solid mp 54-56°: ¹H NMR (CDCl₃) δ 2.94 (t, J_{HF} = 4.5 Hz, CH); ¹⁹F NMR (CDCl₃) ϕ 102 (m, 4 F, α -CF₂), 122.8 (m, 16 F, internal F) and 124.2 ppm (m, 4 F, β -CF₂); IR 3355 (CH), 2200 (C≡C) and 1190 cm⁻¹ (CF₂).

Anal. Calcd for C₁₆H₂F₂₄: C, 29.56; H, 0.31; F, 70.13. Found: C, 29.30; H, 0.31; F, 70.23.

3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Pentadecafluorononyne. To 10.0 g (0.0168 mol) of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluoro-1-iodo-1-(trimethylsilyl)nonene in 60 mL of tetrahydrofuran at -25°C was added, over a period of 10 min, 5.6 mL (0.0505 mol) of DBU. The mixture was stirred at -25°C for 2 h and was then filtered. The precipitate was washed with cold pentane. The combined organic solutions were washed with brine, filtered through basic alumina and distilled to give 3.25 g (39%) of 80% pure (by GC) 3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluorononyne contaminated with silane biproducts (bp 120-155°C). An analytical sample was isolated by GC (78°C): ¹H NMR (CDCl₃) δ 2.93 (t, J = 6 Hz, =CH); ¹⁹F NMR (CDCl₃) ϕ 85.1 (t, J = 10 Hz, 3 F, CF₃) 102.4 (m, 2 F, α -CF₂), 113.4

(m, 2 F, CF_2), 124.2 (m, 6 F, CF_2), 128.0 ppm (m, 2 F, CF_2).

Anal. Calcd for C_9HF_{15} : C, 27.43; H, 0.26. Found: C, 27.51; H, 0.28.

(E)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Pentadecafluoro-1-iodo-1-phenylnonene.

A mixture of 3.0 g (6.0 mmol) of perfluoroheptyl iodide, 0.60 g (6.0 mmol) of phenylacetylene and 0.5 mL of di-*t*-butyl peroxide was sealed in a glass tube under vacuum and was heated for 48 h at 120°C. The product was dissolved in methylene chloride, dried over magnesium sulfate and stripped of solvent to give 3.24 g (89%) of essentially pure (E)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluoro-1-iodo-1-phenylnonene. An analytical sample was isolated by GC: mp 49-51°C; ^1H NMR (CDCl_3) δ 7.20 (s, 5 H, C_6H_5), 6.51 ppm (t, $J_{\text{H},\text{F}} = 12$ Hz, 1 H, CH); ^{19}F NMR (CDCl_3) δ 85.6 (t, 3 F, CF_3) 108.0 (q, 2 F, CF_2), 123.6 (m, 2 F, CF_2), 124.4 (m, 6 F, CF_2), 128.0 ppm (m, 2 F, CF_2).

Anal. Calcd for $\text{C}_{15}\text{H}_6\text{F}_{15}\text{I}$: C, 30.12; H, 1.01; F, 47.65; I, 21.22.

Found: C, 30.18, H, 1.22; F, 47.30; I, 21.10.

1-Phenylperfluorononyne. A solution of 3.0 g (5.04 mmol) of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluoro-1-iodo-1-phenylnonene in 20 mL of dry methylene chloride was added dropwise to a stirred suspension of 1.1 g of potassium *t*-butoxide in 40 mL of dry methylene chloride at -20°C. The mixture was stirred for 1 h at -20°C and for 2 h at 0°C. The mixture was stirred for 1 h with 20 mL of 3 N hydrochloric acid. The organic layer was washed with water and dried over magnesium sulfate. Solvent was removed to give 1.84 g (18%) of essentially pure 1-phenylperfluorononyne. An analytical sample was obtained by GC: ^1H NMR (CDCl_3) δ 7.33 ppm (m, 5 H, C_6H_5); ^{19}F NMR (CDCl_3) δ 84.8 (t, 3 F, CF_3) 100 (t, 2 F, CF_2), 122.8 (m, 2 F, CF_2), 124.0 (m, 6 F, CF_2), 127.6 ppm (m, 2 F, CF_2).

Anal. Calcd for $\text{C}_{15}\text{H}_5\text{F}_{15}$: C, 38.32; H, 1.07; F, 60.61. Found: C, 37.85;

H, 1.14; F, 59.37.

(E,E)-3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluoro-2,9-bis(iodomethylidemethylsilyl)-1,10-bis(trimethylsilyl)-1,9-decadiene. A mixture of 3.7 g (0.0066 mol) of 1,6-diiodoperfluorohexane, 2.3 g (0.0133 mol) of bis(trimethylsilyl)acetylene and 0.5 ml of di-*t*-butyl peroxide was sealed under vacuum in a heavy-walled glass tube and the tube heated at 120°C for 48 h. The mixture was dissolved in 50 mL of methylene chloride, washed with 3-50 mL portions of water, dried over magnesium sulfate, and stripped of solvent with a rotary evaporator to give 4.5 g (75%) of essentially pure product (NMR) as an off-white solid, mp 62-68°C. Recrystallization from methanol CH₃OH afforded an analytical sample mp 68-70°C: ¹H NMR (CDCl₃) δ 6.83 (br s, 2 H, CH), 2.08 (s, 4 H, CH₂I), 0.35 (s, 12 H, CH₃), 0.17 ppm (s, 18 H, CH₃); ¹⁹F NMR (CDCl₃) δ 104.4 (m, 4 F, CF₂), 120.4 (m, 4 F, CF₂), 123.2 ppm (m, 4 F, CF₂).

Anal. Calcd for C₂₂H₃₆F₁₂I₂Si₄: C, 29.54; H, 4.06; I, 28.37. Found: C, 29.38; H, 4.37; I, 27.99.

(E)-3,3,4,4,5,5,5-Heptafluoro-2-(iodomethyl)dimethylsilyl-1-trimethylsilylpentene. By the above procedure, 0.300 g (0.001 mol) of perfluoropropyl iodide, 0.170 g (0.001 mol) of bis(trimethylsilyl)acetylene and 0.25 ml of di-*t*-butyl peroxide gave 0.40 g (84%) of the title compound. An analytical sample was isolated by GC: ¹H NMR (CDCl₃) δ 6.65 (br s, 1 H, CH), 2.07 (s, 2 H, CH₂I), 0.37 (s, 6 H, CH₃), 0.18 ppm (s, 9 H, CH₃); ¹⁹F NMR (CDCl₃) δ 84.8 (t, 3 F, CF₃), 105.2 (d, 2 F, CF₂), 124.8 ppm (s, 2 F, CF₂).

Anal. Calcd for C₁₁H₁₈F₇Si₂: C, 28.33; H, 3.89; F, 28.52; I, 27.21. Found: C, 28.12; H, 3.77; F, 28.52; I, 27.45.

(E)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Pentadecafluoro-2-(iodomethyl)dimethylsilyl-1-trimethylsilylnonene. By the above procedure, 0.50 g (0.001 mol) of perfluoroheptyl iodide, 0.170 g (0.001 mol) of bis(trimethylsilyl)acetylene and 0.25 mL of di-t-butyl peroxide gave 0.56 g (85%) of the title compound. An analytical sample was isolated by GC: ^1H NMR (CDCl_3) δ 6.71 (br s, 1 H, CH), 2.05 (s, 2 H, CH_2I), 0.33 (s, 6 H, CH_3), 0.18 ppm (s, 9 H, CH_3); ^{19}F NMR (CDCl_3) δ 85.2 (t, 3 F, CF_3), 104.4 (m, 2 F, CF_2), 120.4 (m, 2 F, CF_2), 123.6 (m, 6 F, CF_2), 127.6 ppm (m, 2 F, CF_2); IR (film) 3010 (CH_3), 1200 cm^{-1} (CF_2).

Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{F}_{15}\text{ISi}_2$: C, 27.04; H, 2.72; F, 42.77; I, 19.04. Found: C, 27.14; H, 2.78; F, 42.54; I, 18.91.

1,12-Bis(trimethylsilyl)perfluoro-1,11-dodecadaiyne. A heavy-walled silylated glass tube, loaded with 4.2 g (0.025 mol) of bis(trimethylsilyl)acetylene, 5.0 g (0.00765 mol) of 1,8-diiodoperfluorooctane and 0.024 g (0.0001 mol) of iodine, was evacuated at -78°C , filled with nitrogen, and sealed. The tube was heated at 200°C for 57 h. Bulb-to-bulb distillation at $90\text{--}110^\circ\text{C}$ (0.02 to 0.05 mm) gave 3.91 g (86%) of 1,12-bis(trimethylsilyl)perfluorododeca-1,11-diyne as a pink liquid (>97% pure by GC). An analytical sample was obtained by preparative GC at 125°C : ^1H NMR (CDCl_3 , CH_2Cl_2) δ 0.37 ppm (s, - SiCH_3); ^{19}F NMR (CDCl_3 , CFCl_3) δ 100.8 (m, 4 F, - CF_2 , $\text{C}\equiv\text{C}$), 123.2 (m, 8 F, CF_2), 124.3 ppm (m, 4 F, CF_2); IR (film) 3000 (SiH_3), 2940 (SiMe_3), 2230 ($\text{C}\equiv\text{C}$), 1200 cm^{-1} (CF_2).

Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{F}_{16}\text{Si}_2$: C, 36.37; H, 3.05; F, 51.13. Found: C, 36.18; H, 3.00; F, 50.90.

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-Hexadecafluoro-1,11-dodecadiyne. A mixture of 38.4 g (0.0646 mol) of 1,12-bis(trimethylsilyl)perfluoro-1,11-dodecadiyne, 60.7 g (0.646 mol) of potassium fluoride dihydrate and 150 mL of methanol was stirred at room temperature for 20 h. Saturated sodium chloride solution and ether were added and the phases were separated. The aqueous phase was extracted several times with ether and the combined ether solutions were washed with brine, dried over magnesium sulfate and distilled to give 23.0 g (79%) of the diacetylene as a pale pink liquid: bp 85-90°C (30 mm); ^1H NMR (CDCl_3) δ 2.94 ppm (t, $J_{\text{HF}} = 4.5$ Hz, $\text{C}\equiv\text{C}-\text{H}$); ^{19}F NMR (CDCl_3) δ 102.0 (m, 4 F, $\text{CF}_2\text{C}\equiv$), 122.8 (m, 8 F, $\equiv\text{CF}_2\text{CF}_2$), 124.0 ppm (m, 4 F, $\equiv\text{CCF}_2\text{CF}_2\text{CF}_2\text{CF}_2$); IR (film) 3355 (C-H), 2195 (C≡C), 1190 cm^{-1} (CF_2).

Anal. Calcd for $\text{C}_{12}\text{H}_2\text{F}_{16}$: C, 32.02; H, 0.45; F, 67.53. Found: C, 32.44; H, 0.55; F, 65.56.

1-Trimethylsilylperfluorononyne. A mixture of 11.8 g (0.070 mmol) of bis(trimethylsilyl)acetylene, 30.0 g (0.060 mol) of perfluoropropyli iodide and 0.022 g (0.00009 mol) of iodine was heated for 71 h at 200°C in a Monel bomb. The product was dissolved in methylene chloride, washed with sodium thiosulfate solution, dried and distilled to give 18.4 g (65%) of 1-trimethylsilylnonyne, bp 39-40°C (0.27-0.37 mm): ^1H NMR (CDCl_3 , CH_2Cl_2) δ 0.15 ppm (s, 9 H, SiCH_3); ^{19}F NMR (CDCl_3) δ 85.6 (t, $J = 10$ Hz, 3 F, CF_3), 101.2 (t, $J = 8$ Hz, 2 F, $-\text{CF}_2\text{C}\equiv$), 122.8 (m, 2 F, CF_2), 124.0 (m, 6 F, CF_2), 127.6 ppm (m, 2 F, CF_2); IR (film) 3000 (SiCH_3), 2940 (SiCH_3), 2230 (C≡C), 1200 (CF_2), 860 cm^{-1} (SiCH_3).

Anal. Calcd for $\text{C}_{12}\text{H}_9\text{F}_{15}\text{Si}$: C, 30.91; H, 1.94. Found: C, 30.98; H, 1.68.

1-Trimethylsilylperfluorooctyne, 1-Trimethylsilylperfluorodecyne and 1-Trimethylsilylperfluorododecyne. A commercial mixture of perfluoroalkyl iodides ($\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_{2-5}\text{-I}$, Hoechst perfluoroalkyljodid 25) was subjected to the above reaction. Thus, 26.7 g of the mixture was heated with 10.0 g of bis-(trimethylsilyl)acetylene and 0.12 g of iodine for 66 h at 200°C. Kugelrohr distillation (25-75°C, 0.1-0.02 mm) gave 21.7 g of a mixture of the trimethylsilylacetylenes. Samples of the three major components were isolated by preparative GC at 80°C. 1-Trimethylsilylperfluorooctyne was a colorless liquid:

$^1\text{H NMR}$ (CDCl_3) δ 0.44 ppm (s, $-\text{CH}_3$); $^{19}\text{F NMR}$ (CDCl_3) ϕ 86.1 (m, 3 F, $-\text{CF}_3$), 102.1 (t, $J = 11$ Hz, 2 F, $-\text{CF}_2\text{C}\equiv$), 124.4 (m, 2 F, $-\text{CF}_2\text{CF}_2\text{C}\equiv$), 125.6 (m, 4 F, $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2-$), 129.0 ppm (m, 2 F, CF_3CF_2-); IR (film) 3000 (C-H), 2230 (C=C), 1200 (CF_2), 860 cm^{-1} (SiCH_3).

Anal. Calcd for $\text{C}_{11}\text{H}_9\text{F}_{13}\text{Si}$: C, 31.74; H, 2.18; F, 59.33. Found: C, 31.60; H, 2.22; F, 59.12.

1-Trimethylsilylperfluorodecyne was a colorless liquid: $^1\text{H NMR}$ (CDCl_3) δ 0.35 ppm (s, CH_3); $^{19}\text{F NMR}$ (CDCl_3) ϕ 86.2 (t, $J = 10$ Hz, 3 F, $-\text{CF}_3$), 102.2 (t, $J = 11$ Hz, 2 F, $-\text{CF}_2\text{C}\equiv$), 125.2 (m, 10 F, $\text{CF}_3\text{CF}_2(\text{CF}_2)_5$), 129.2 ppm (m, 2 F, CF_3CF_2); IR (film) 3010 (C-H), 2250 (C=C), 1200 (CF_2) 860 cm^{-1} (SiCH_3).

Anal. Calcd for $\text{C}_{13}\text{H}_9\text{F}_{17}\text{Si}$: C, 30.24; H, 1.76; F, 62.56. Found: C, 30.13; H, 1.77; F, 62.80.

1-Trimethylsilylperfluorododecyne was a colorless liquid: $^1\text{H NMR}$ (CDCl_3) δ 0.40 ppm (s, $-\text{CH}_3$); $^{19}\text{F NMR}$ (CDCl_3 , CFCl_3) ϕ 86.0 (t, $J = 10$ Hz, 3 F, $-\text{CF}_3$), 102.0 (m, 2 F, $-\text{CF}_2\text{C}\equiv$), 124.8 (m, 14 F, $-\text{CF}_2$), 128.9 ppm (m, 2 F,

$\text{-CF}_2\text{CF}_3$); IR (film) 3020 (CH), 2250 (C=C), 1200 (CF₂), 860 cm⁻¹ (SiCH₃).

Anal. Calcd for C₁₅H₉F₂₁Si: C, 29.23; H, 1.47; F, 64.74. Found: C, 28.59; H, 1.53; F, 63.71.

Reaction of 1-(Trimethylsilyl)perfluorononyne with Methanol. A mixture of 0.40 g (0.86 mmol) of 1-(trimethylsilyl)perfluorononyne, 0.6 g (4.3 mmol) of anhydrous potassium carbonate and 1.5 ml. of methanol was stirred at room temperature under nitrogen for 15 h. Water was added and the product was extracted into ether. The ether solution was washed with water, dried over magnesium sulfate and stripped of solvent to give 0.33 g of a 7.3:1 mixture (by GC) of 1,1-dimethoxy-3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluorononane (73%) and 1-methoxy-3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluorononene (1%). The mixture was separated by preparative GC at 60°C. The olefin consisted of a 5.8:1 mixture of Z and E isomers; an analytical sample of the major isomer was isolated as a colorless liquid: ¹H NMR (CDCl₃) δ 6.31 (d t, J_{HH} = 7.2 Hz, J_{HF} = 1.8 Hz, 1 H, C=CHOMe), 4.44 (d t, J_{HH} = 7.2 Hz, J_{HF} = 15 Hz, 1 H, CF₂CH=), 3.77 ppm (s, 3 H, OCH₃); ¹⁹F NMR (CDCl₃) δ 85.2 (t, J = 10 Hz, 3 F, CF₃), 108.8 (q, J = 23 Hz, 2 F, CF₂CH=), 124.2 (m, 6 F, CF₂), 125.6 (m, 2 F, CF₂), 128.0 (m, 2 F, CF₂).

Anal. Calcd for C₁₀H₅F₁₅O: C, 28.19; H, 1.18. Found: C, 28.29; H, 1.15.

The dimethoxy compound was isolated as a colorless liquid: ¹H NMR (CDCl₃) δ 4.76 (t, J = 6 Hz, 1 H, CH₂CH(OMe)₂), 3.39 (s, 6 H, OCH₃), 2.40 ppm (m, 2 H, CF₂CH₂); ¹⁹F NMR (CDCl₃) δ 85.2 (t, J = 10 Hz, 3 F, CF₃) 124.2 (m, 10 F, CF₂), 128.0 ppm (m, 2 F, CF₂).

Anal. Calcd for C₁₁H₉F₁₅O₂: C, 28.84; H, 1.98; F, 62.20. Found: C, 28.62; H, 1.86; F, 62.39.

Reaction of 1,4-Diodoperfluorobutane with Bis(trimethylsilyl)acetylene.

A mixture of 41 g (0.024 mol) of bis(trimethylsilyl)acetylene, 10.0 g (0.022 mol) of 1,4-diodoperfluorobutane and 0.11 g (0.00044 mol) of iodine was heated by the above procedure for 70 h at 200°C. Bulb-to-bulb distillation (30-50°C, 0.12 mm, -78°C receiver) gave 7.6 g (81%) of the cyclic adduct as a purple liquid. An analytical sample was isolated by preparative GC (115°C):

^1H NMR (CDCl_3) δ 0.50 ppm (t, $J_{\text{HF}} = 1$ Hz, 9 H, SiCH_3), ^{19}F NMR (CDCl_3) 104.4 (m, 2 F, CF_2), 113.6 (m, 2 F, CF_2), 135.2 (m, 2 F, CF_2), 136.8 ppm (m, 2 F, CF_2); IR (film) 3000 (SiMe_3), 2940 (SiMe_3), 1590 cm^{-1} (C=C).

Anal. Calcd for $\text{C}_9\text{H}_9\text{F}_8\text{Si}$: C, 25.49; H, 2.14; F, 35.82; I, 29.92.

Found: C, 25.27; H, 2.11; F, 36.02; I, 30.27.

Reaction of 1,6-Diodoperfluorohexane with Bis(trimethylsilyl)acetylene.

A mixture of 1.24 g (0.0073 mol) of bis(trimethylsilyl)acetylene, 2.0 g (0.0036 mol) of 1,6-diodoperfluorohexane and 0.12 g (0.0005 mol) of iodine was heated by the above procedure for 24 h at 200°C. Bulb-to-bulb distillation of the product (70-84°C, 0.02-0.03 mm) gave 1.09 g of liquid shown by GC to contain 0.65 g (36%) of 1,10-bis(trimethylsilyl)perfluoro-1,9-decadiyne and 0.22 g (12%) of the cyclic adduct (see discussion). Analytical samples were isolated by GC at 105°C. The latter was isolated as a pale orange liquid:

^1H NMR (CDCl_3) δ 0.55 ppm (t, $J = 1$ Hz, $-\text{Si}(\text{CH}_3)_3$); ^{19}F NMR (CDCl_3) ϕ 97.6 (m, 2 F, $\text{CF}_2\text{C}=\text{C}$, 105.4 (m, 2 F, $\text{CF}_2\text{C}=\text{C}$), 124.2 (m, 2 F, CF_2), 126.5 (m, 2 F, CF_2), 129.6 (m, 2 F, CF_2), 130.4 ppm (m, 2 F, CF_2); IR (film) 3000 ($-\text{SiMe}_3$), 2940 ($-\text{SiMe}_3$), 1550 cm^{-1} (C=C).

Anal. Calcd for $\text{C}_{11}\text{H}_9\text{F}_{12}\text{Si}$: C, 25.20; H, 1.73; F, 43.49; I, 24.21.

Found: C, 24.97; H, 1.70; F, 43.62; I, 24.38.

1,10-bis(trimethylsilyl)perfluoro-1,9-decadiyne was isolated as a pale pink liquid; ^1H NMR (CDCl_3) δ 0.27 ppm (s, 18 H, $-\text{SiCH}_3$); ^{19}F NMR (CDCl_3) δ 101.3 (m, 4 F, $-\text{C}\equiv\text{C}-\text{CF}_2$), 123.4 (m, 4 F, CF_2), 124.8 ppm (m, 4 F, CF_2); IR (film) 3000 (SiMe_3), 2940 (SiMe_3), 2220 (C≡C), 1200 (CF_2), 860 cm^{-1} (SiMe_3).

Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{F}_{12}\text{Si}_2$: C, 38.86; H, 3.67; F, 46.11. Found: C, 38.72; H, 3.67; F, 46.25.

References

1. This work was supported by the Office of Naval Research.
2. Haszeldine, R. N. J. Chem. Soc. 1950, 3037.
3. Ibid. 1951, 588.
4. Haszeldine, R. N.; Leedham, K. J. Chem. Soc. 1952, 3483.
5. Henne, A. L.; Mager, M. J. Am. Chem. Soc. 1951, 73, 1042.
6. LeBlanc, M.; Santini, G.; Jeanneaux, F.; Riess, J. G. J. Fluorine Chem. 1976, 7, 525.
7. Bedford, C. D.; Baum, K. J. Org. Chem. 1980, 45, 347.
8. Knunyants, I. L.; Khriakyan, S. P.; Zeifman, Yu. V.; Shokina, V. V. Izv. Akad. Nauk SSSR, Ser. Khim. 1964, 384.
9. T. Takahashi, S.; Kuroyanagi, Y.; Sonogashira, K.; Nagitara, N. Synthesis 1980, 627.
10. Austin, W. B.; Bilow, N.; Kelleghan, W. J.; Law, K. S. Y. J. Org. Chem. 1981, 46, 2280.
11. Zweifel, G.; Murray, R. E.; On, H. P. J. Org. Chem. 1981, 46, 1292.
12. Brace, N. O.; Van Elswyk, J. E. J. Org. Chem. 1976, 41, 766.
13. Freidlina, R. Kh.; Terent'ev, A. B. Acc. Chem. Res. 1977, 10, 5; Piccardi, P.; Massardo, P.; Modena, M.; Santoro, E. J. Chem. Soc. Perkin I 1974, 1848.
14. Haszeldine, R. N. J. Chem. Soc. 1952, 3496.

TECHNICAL REPORT DISTRIBUTION LIST, 356A

<u>No.</u>	<u>Copies</u>	<u>No.</u>	<u>Copies</u>
Dr. Stephen E. Carr Department of Materials Science Northwestern University Evanston, Illinois 60201	1	Picatinny Arsenal Attn: A. M. Anzalone, Building 3401 SMUPA-FR-M-0 Dover, New Jersey 07801	1
Dr. M. Broadhurst Bulk Properties Section National Bureau of Standards U.S. Department of Commerce Washington, D.C. 20234	2	Dr. J. K. Gillham Department of Chemistry Princeton University Princeton, New Jersey 08540	1
Professor G. Whitesides Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139		Dr. E. Baer Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106	1
Dr. D. R. Uhlmann Department of Metallurgy and Material Science Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Dr. K. D. Pae Department of Mechanics and Materials Science Rutgers University New Brunswick, New Jersey 08903	1
Naval Surface Weapons Center Attn: Dr. J. M. Augl, Dr. B. Hartman White Oak Silver Spring, Maryland 20910	1	NASA-Lewis Research Center Attn: Dr. T. T. Serofini, MS-49-1 21000 Brookpark Road Cleveland, Ohio 44135	1
Dr. G. Goodman Globe Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1	Dr. Charles H. Sherman Code 121 Naval Underwater Systems Center New London, Connecticut 06320	1
Professor Sacsuo Ishida Department of Macromolecular Science Case-Western Reserve University Cleveland, Ohio 44106	1	Dr. William Risen Department of Chemistry Brown University Providence, Rhode Island 02192	1
Dr. David Soong Department of Chemical Engineering University of California Berkeley, California 94720	1	Dr. Alan Gent Department of Physics University of Akron Akron, Ohio 44304	1
Dr. Curtis W. Frank Department of Chemical Engineering Stanford University Stanford, California 94305		Mr. Robert W. Jones Advanced Projects Manager Hughes Aircraft Company Mail Station J 132 Culver City, California 90230	1

TECHNICAL REPORT DISTRIBUTION LIST, 356A

<u>No.</u>	<u>Copies</u>	<u>No.</u>	<u>Copies</u>
Dr. C. Giorgi ITT Research Institute 10 West 35 Street Chicago, Illinois 60616	1	Dr. J. A. Manson Materials Research Center Lehigh University Bethlehem, Pennsylvania 18015	1
Dr. R. S. Roe Department of Materials Science and Metallurgical Engineering University of Cincinnati Cincinnati, Ohio 45221	1	Dr. R. F. Helreich Contract RD&E Dow Chemical Co. Midland, Michigan 48640	1
Dr. Robert E. Cohen Chemical Engineering Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Dr. R. S. Porter Department of Polymer Science and Engineering University of Massachusetts Amherst, Massachusetts 01002	1
Dr. T. P. Coalon, Jr., Code 3622 Sandia Laboratories Sandia Corporation Albuquerque, New Mexico	1	Professor Garth Wilkes Department of Chemical Engineering Virginia Polytechnic Institute and State University Blacksburg, Virginia 24061	1
Dr. Martin Kaufman, Head Materials Research Branch, Code 4542 Naval Weapons Center China Lake, California 93555	1	Dr. Kurt Baum Fluorochex Inc. 680 S. Ayon Avenue Azusa, California 91702	1
Professor S. Sencur Department of Electrical Engineering Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Professor C. S. Paik Sung Department of Materials Sciences and Engineering Room 8-109 Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1
Dr. T. J. Reinhart, Jr., Chief Composite and Fibrous Materials Branch Nonmetallic Materials Division Department of the Air Force Air Force Materials Laboratory (AFSC) Wright-Patterson AFB, Ohio 45433	1	Professor Brian Newman Department of Mechanics and Materials Science Rutgers, The State University Piscataway, New Jersey 08834	1
Dr. J. Lando Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106	1	Dr. John Lundberg School of Textile Engineering Georgia Institute of Technology Atlanta, Georgia 30332	1
Dr. J. White Chemical and Metallurgical Engineering University of Tennessee Knoxville, Tennessee 37916	1		

TECHNICAL REPORT DISTRIBUTION LIST, GAN

<u>No.</u>	<u>Copies</u>	<u>No.</u>	<u>Copies</u>
Office of Naval Research Attn: Code 472 300 North Quincy Street Arlington, Virginia 22217		U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
ONR Western Regional Office Attn: Dr. L. J. Marcus 1030 East Green Street Pasadena, California 91106	2	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Eastern Regional Office Attn: Dr. L. E. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20330	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Dr. Fred Sealfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST, GEN

No.
Copies

Mr. Vincent Schaper NTNSRDC Code 2803 Annapolis, Maryland 21402	1
Mr. A. M. Anzalone Administrative Librarian PLASTEC/AERADCOM Bldg 3401 Kaser, New Jersey 07801	1